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MEMORANDUM**

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(NASA-TM-X-71676) PMR POLYIMIDES:
PROCESSABLE HIGH TEMPERATURE COMPOSITE
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**PMR POLYIMIDES - PROCESSABLE HIGH TEMPERATURE
COMPOSITE MATRIX RESINS**

W. E. Winters
TRW Equipment
and
T. T. Serafini
Lewis Research Center
Cleveland, Ohio

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PMR POLYIMIDES - PROCESSABLE
HIGH TEMPERATURE COMPOSITE MATRIX RESINS

W. E. Winters - TRW Equipment, Cleveland, Ohio

T. T. Serafini - NASA-Lewis Research Center

Abstract

Processing reproducibility and versatility were demonstrated for producing addition-cured polyimide/graphite fiber composites using a unique in situ polymerization of monomeric reactants directly on the fiber surface. The polymers so derived, designated PMR polyimides, can be fabricated into composite structures by laminating, random fiber molding or autoclave curing. Composites were determined to be thermally stable and retain useful properties after extended exposures at 550°F to 650°F. The material and fabrication capability were demonstrated by the fabrication and evaluation of prototype complex fan blades.

1. INTRODUCTION

Advanced fiber composites are becoming accepted as engineering materials for aeronautical and aerospace structural applications. The most widely used matrix materials are epoxy resins. The relatively low use temperature of epoxy resins has restricted the application of epoxy resin/fiber composites to temperatures below 350°F. Also, environmental effects on high temperature mechanical properties have restricted their application even further. High temperature resistant polymers, that is, polymers capable of withstanding temperatures up to 600°F for extended time periods, have been available since the early 1960's. However, because of their intractable nature, their potential as matrix resins has not been realized.

In 1968 investigators at the Systems Group of TRW Inc., under NASA sponsorship, developed an approach to prepare polyimides by means of an addition-reaction⁽¹⁾. Low molecular weight amide-acid prepolymers end-capped with norbornene rings were found to polymerize without the evolution of volatile material.

Studies conducted at the NASA-Lewis Research Center led to the development of a vastly improved method for preparing addition-cured polyimides^{(2), (3)}. In this approach, in situ Polymerization of Monomer Reactants occurs on the surface of the reinforcing fibers. The polymers derived using the techniques are designated PMR polyimides.

Studies reported in references (4) and (5) were undertaken by TRW Equipment

of TRW Inc. to establish a broad technology base for PMR polyimides. These studies included work to define PMR polyimide/graphite fiber processing methodology and the characterization of composite mechanical property retention characteristics at elevated temperatures over extended time periods. This work culminated in the fabrication of complex fan blades designed for operation at blade tip speeds of 2200 ft/sec.

This report reviews the PMR polyimide composite studies conducted at the NASA-Lewis Research Center and TRW Equipment. Particular emphasis is given to the recent studies⁽⁵⁾⁽⁶⁾ which describe the processing versatility and use of PMR polyimides to fabricate composite fan blades.

2. MATERIALS

Aromatic polyimides are generally formed by the reaction of aryl diamines with aromatic dianhydrides or the dimethyl esters of aromatic tetracarboxylic acids. Following impregnation of reinforcing fibers with a "polyimide varnish" solution, mild heating (staging) of the prepreg, to achieve an acceptable level of volatiles, results in the formation of molecular structures which adversely affect the removal of volatile materials produced during final curing under pressure. Addition polyimides of the "A" type⁽¹⁾ are achieved through the polymerization of low molecular weight prepolymers end-capped with norbornene groups without the evolution of volatile materials. PMR polyimides are also cured by an addition reaction of norbornene groups. The structures of the monomers, intermediate and cured polymer are shown in Figure 1. Specifically, the reactants used to produce the PMR polyimides used in this study were as follows:

- (1) 4,4'-methylenedianiline (MDA)
- (2) Monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE)
- (3) Dimethyl ester of 3,3',4,4'-ben-

zophenonetetracarboxylic acid (BTDE)

The MDA and NE are commercially available crystalline materials while the BTDE is readily obtained by refluxing the dianhydride of benzophenonetetracarboxylic acid (BTDA) in methanol. All reactants are readily soluble in anhydrous methanol at room temperature. Concentrated (25-60 w/o), low viscosity (20-60 cps) solutions which are stable for at least two weeks can be prepared. Because solution preparation merely involves simple mixing, monomer solutions can be prepared daily so that storage or shelf life problems are non-existent with PMR polyimides. Also, because of the ease of solution preparation, formulated molecular weight (FMW) variations are readily achieved. FMW's ranging from 1000 to 1900 have been studied. In general, higher molecular weight resin is characterized by lower resin flow during processing while lower FMW, having higher alicyclic content and crosslink density, exhibits somewhat lower thermooxidative stability and slightly greater stiffness. Following are the number of moles of the constituents used for two PMR polyimides of different FMW:

FMW	NE	MDA	BTDE
1100	2	2.260	1.260
1500	2	3.087	2.087

The majority of effort with PMR polyimides has been devoted to composites using graphite fiber reinforcements including both high strength (HT-S) and high modulus (HM-S) type fibers. However, sound (void-free) composites have been produced using "E" and "S" glass reinforcements as well.

3. PROCESSING VERSATILITY

3.1 PROCESSING PARAMETERS

The basic processing steps for producing composites of PMR polyimides are much the same as for other "A" type polyimides. However, as indicated in

Table I, a high degree of processing flexibility exists. The fiber collimation and impregnation operations are conventional except that the low viscosity solution assures total impregnation of fiber bundles and fiber wetting. Staging to reduce volatiles for appropriate tack and drape properties can be achieved at room temperature or by mild heating. Imidization can be accomplished on a pre-stacked laminate either in an air-circulating oven, in the final molding tool, or on the mandrel. Higher temperatures and longer imidization times result in reduced resin flow in final cure.

The final curing operation is performed by inserting the imidized preform in a warm or hot tool or by using a tool or mandrel equipped with heaters. One of the particularly advantageous characteristics of the material is that, with lower insertion temperatures, a reasonable amount of time can elapse before pressure application, thereby eliminating operator judgment factors. Cure is achieved in one hour at 600°F. Postcure is essential where maximum use temperature and exposure time requirements demand ultimate performance. However, unduly long or complicated programmed temperature rise schedules are not required.

3.2 PROCESSING AND FMW EFFECTS

The selection of a resin matrix system for a complex hardware configuration of composite material is dependent not only on the ability of the resin matrix to translate fiber efficiency and achieve the required resistance to thermal degradation, but upon the ability of the material to be fabricated into a sound structure with reasonable ease. Some applications and processing methods demand more resin flow to achieve full composite consolidation than do others. The versatility of FMW variation in PMR polyimides allows a wide range of resin flow. Figure 2 shows that 20% resin expulsion occurs at an FMW of 1000. Some loss in thermo-oxidative stability of lower molecular weight polymers is

exhibited at 550°F (Figure 3) while at 450°F insignificant loss in weight is observed to at least 600 hour exposure.

The variation of composite flexural strength (normalized for 0.55 V_f) with molecular weight using HT-S graphite fiber is illustrated in Figure 4. Room temperature strength ranged from 223 ksi at FMW of 1000 to 200 ksi at FMW 1500. Retention of strength at 450°F ranged from 75 to 88% and at 550°F from 70-78%. Elevated temperature tests were conducted after 15 minutes exposure at the indicated temperatures.

It is interesting to note in Figure 4 a decrease in strength at higher molecular weight levels. It is felt that the data reflect the effect of matrix modulus as well as temperature. The lower FMW, having a higher alicyclic, higher cross link density would be expected to exhibit a higher neat resin modulus and lower thermal stability. The room temperature results thus reflect the effect of matrix modulus while the elevated temperature strengths reflect both matrix modulus and temperature effects.

3.3 FABRICATION METHODS

Fabrication of PMR polyimide composites by compression molding or conventional laminating techniques is straightforward and reproducible. A pre-imidized stack or preform is inserted into a closed die or heated platens, and after a short dwell period to assure through-heating, pressures of 500 to 1000 psi are applied. The high melt viscosity of higher FMW formulations preclude fiber wash or excess resin expulsion.

Although most of the composite fabrication to date has been by closed die molding of continuous fiber composite, other approaches also have been investigated. A highly successful method has been random fiber molding using a chopped graphite fiber/PMR-15 molding compound. In this case, collimated fiber prepreg was merely chopped to the

desired fiber length. Figure 5 illustrates a 2-3/4 inch diameter puck molding with legs of varying size which is used to investigate the fiber/resin flow characteristics of the material. In this case, only the smallest (1/4 inch diameter) of the three legs did not completely fill. Distribution of resin and reinforcement was, however, excellent in all cases. The photomicrograph of the body of the puck illustrates a completely void-free structure while the mechanical properties are typical of a good quality molding compound incorporating 3/8 inch lengths of high strength graphite fiber.

Another fabrication approach for which feasibility has been demonstrated with PMR polyimides is autoclave curing. Figure 6 illustrates two typical photomicrographs of autoclave cured (200 psi) unidirectional graphite composites indicating a void content of 2.7%. It will be noted that the porosity is primarily interply suggesting entrapped air rather than reaction by-product volatiles. Optimization studies are continuing through cure schedule and FMW modifications and there is high confidence that even lower void content composites can be reproducibly achieved.

The addition type polymerization mechanism of PMR polyimides coupled with extended gelation times and available resin flow permit fabrication of composites of essentially unlimited thickness. Figure 7 illustrates a fully dense, half-inch thick laminate. Both unidirectional and oriented composites of this dimension and thicker have been produced without difficulty. It is concluded that PMR polyimides are adaptable to a variety of fabrication methods and hardware applications.

4. COMPOSITE PROPERTIES

The evaluation of PMR polyimide composites made from PMR-15 (polyimide of FMW = 1500) has been extensive. In general, excellent translation of fiber

properties is achieved with retention of properties for extended air aging up to 600°F. Particular emphasis has been placed on effects of processing on mechanical performance. Table II presents room and short term 600°F properties for two distinctly different processing conditions. The insertion temperature refers to the tool or platen temperature into which the imidized preform is charged. Essentially, no difference in properties is observed between the two methods. The need for postcure to achieve best 600°F properties is dramatically evident. However, for application at lower temperatures (e.g., 450°F), large percentages of the room temperature properties are retained without the need for postcure as illustrated in Table III.

Long term, elevated temperature aging effects in air environment are demonstrated in Figure 8. At 550°F fully post-cured HM-S graphite composites experience essentially no thermo-oxidative degradation for durations of at least 1000 hours while at 600°F the weight loss is significant but not excessive. Serious degradation is experienced with extended air exposure at 650°F. Relating weight loss to mechanical performance, 60-80% of the unaged flexure strength is retained after 600°F/1000 hours exposure. At 650°F composites maintain 90% of their strength at 50 hours exposure indicating that short duration excursions to higher than normal or desired temperature ranges would not be catastrophic to a composite structure.

5. HARDWARE APPLICATION

One of the most rewarding aspects of the PMR polyimide development has been the success achieved in fabrication of prototype hardware. Selected for the demonstration was the ultra-high tip speed blade illustrated in Figure 9. This blade is perhaps the most complex, most highly loaded rotating airfoil ever developed. The design was created by

Pratt and Whitney Aircraft, East Hartford, Connecticut under Contract (NAS3-15335) from NASA-Lewis; the tooling and fabrication development were conducted at TRW Equipment.

The purpose of the blade program is to investigate the aerodynamics of airfoil designs at speeds never before evaluated. The blade rotates at over 15,000 rpm at tip speeds of 2200 ft/sec. Because of the very high stresses involved in the centrifugal and aerodynamic fields, no homogeneous material could survive and the use of high specific strength and stiffness resin composites was mandatory.

The blade is about eleven inches long and eight inches in chord at the tip. Composite thickness varies from over one-half inch at the root to about 0.022 inch at the leading edge. The reinforcement is HT-S graphite fiber and the construction is of varying fiber orientations to achieve the required radial and torsional strengthening and stiffening. The composite structure consists of 77 plies of five and 10 mil material in a complex arrangement of computer developed ply shapes. The root is a splayed fiber construction with metallic wedges and pressure pads.

The blades were compression molded in a simply constructed but complex configured closed die fabricated to close tolerances. The tool was mounted in a hydraulic platen press capable of applying 800 psi on the 75 in² of projected blade area. Imidization was conducted in the tool and the fully imidized preform was molded using the 450°F insertion cycle described earlier.

To date, six of these blades have been produced using PMR-15 polyimide resin matrix. The fabrication was straightforward and no difficulties were encountered using the imidization and cure schedules developed on flat laminates.

The prepreg used in the blade fabrication was prepared by drum winding with

careful control of ply thickness. Since dimensional tolerance of thickness on the finished item is approximately $\pm 1\%$, extreme ply thickness control was essential. Although low resin flow was obtained in the molding operation, the reproducibility of final blade weight and thickness was excellent. Post-mold evaluation by ultrasonic C scan and radiography indicated a sound composite structure.

Several of the blades were spin tested singly in a counter balanced wheel. One blade survived a particularly harsh set of testing conditions. After incremental excursions up to full speed with ultrasonic evaluation after each increment, the blade was subjected to low cycle fatigue (LCF) by spinning up to 100% speed fifty times. This was followed by ten million cycles in high cycle fatigue in first bending mode. Finally, an additional ten cycles in LCF were performed prior to final evaluation. The blade after test was intact although some amount of delamination and cracking had been experienced.

As a result of the success achieved with a limited number of blade trials with a new material, the PMR type polyimide has been selected as the bill-of-material. The program is continuing with additional blade development and design optimization. Ultimately, sufficient blades will be fabricated for a single wheel-set which then will be evaluated for aerodynamic performance.

6. CONCLUDING REMARKS

The *in situ* polymerization of monomer reactants (PMR) approach to producing polyimide polymers has been demonstrated to be a viable concept for generating composite structures exhibiting superior high temperature properties, lower cost and greater safety. Of particular advantage are the ease of resin preparation, low viscosity solutions assuring reinforcement wet-out, and a variety of cure schedules which are

independent of operator judgment. The readily prepared compositions can be tailor made to a particular requirement or processing method. Fabrication approaches which can be used include lamination, random fiber molding and autoclave curing. The PMR approach has been demonstrated to be capable of producing highly sophisticated hardware of high quality and PMR polyimides can be considered at this time as available engineering materials of construction.

REFERENCES

1. Burns, E. A., Lubowitz, H. R., Jones, J. F., "Investigation of Resin Systems for Improved Ablative Materials," NASA Report No. CR-72460, October 1968.
2. Serafini, T. T., Delvigs, P., and Lightsey, G. R., "Thermally Stable Polyimides from Solutions of Monomeric Reactants," J. Appl. Polym. Sci., Vol. 16, No. 4, April 1972, pp. 905-915.
3. Delvigs, P., Serafini, T. T., Lightsey, G. R., "Addition-Type Polyimides from Solutions of Monomeric Reactants," NASA Technical Note TN D-6877, August 1972.
4. Cavano, P. J., "Resin/Graphite Fiber Composites," NASA CR-121275, March 1974.
5. Cavano, P. J., "Resin/Graphite Fiber Composites," NASA CR-134727, December 1974.
6. Serafini, T. T. and Vannucci, R. D., "Tailor Making High Performance Graphite Fiber Reinforced PMR Polyimides," NASA TM X-71616, 30th Symposium, Soc. Plastics Industry, Wash., D.C., February 1975.

BIOGRAPHIES

Mr. William E. Winters received the Bachelor of Science degree in Chemical Engineering at Case Institute of Technology which has been augmented with graduate work in polymers and composites. He is the Section Manager of the Resin Composites Section in the Materials Technology Department of TRW Equipment, Cleveland, Ohio. Experience includes over 15 years in ablative and structural composite materials and process development.

Dr. Tito T. Serafini is presently Head of the Polymer Matrix Composite Section of the NASA-Lewis Research Center where he has been since 1963. He received his B.S. in Chemical Engineering, M.S. and Ph.D. from Case Institute of Technology; was a member of the Case Staff in 1961 and received a post-doctoral fellowship from the University of Turin (Italy) in 1962. His current research is in the areas of polymer synthesis and composite fabrication and characterization.

TABLE I
BASIC PMR COMPOSITE PROCESSING

1. Collimation and Impregnation
50% Solids Solution
Air or IR Dry
Oven Stage to Desired Tack/Drape
2. Imidize
Oven or Tool
Temperature 250° to 400°F
Time 1 to 3 hours
3. Mold
Insert Preform Hot 450° to 600°F
Dwell 30 seconds to 10 minutes
Pressure 200 to 1000 psi
Cure Temperature 600°F
Time 1 hour
4. Post Cure
Temperature 650°F
Time 16 hours

TABLE II
COMPOSITE PROPERTIES VS. PROCESSING CONDITIONS
MATERIAL: PMR-15/HM-S

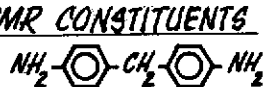
Processing Insertion Temperature Dwell Post Cure	450°F		600°F	
	10 min		30 sec	
	None	650°F/16 hr	None	650°F/16 hr
Properties at Room Temperature				
Flexure Str., ksi	196	-	183	-
Flexure Mod., msi	25.5	-	26.9	-
Shear Str., ksi	8.8	-	8.5	-
at 600°F				
Flexure Str., ksi	-	134	70	160
Flexure Mod., msi	-	22.1	15.2	25.2
Shear Str., ksi	-	6.6	3.2	6.4

TABLE III
ELEVATED TEMPERATURE PROPERTIES OF
NON-POSTCURED PMR-15/HT-S LAMINATES

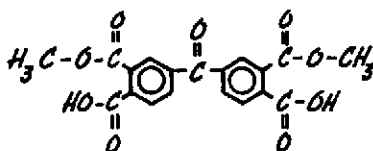
	72°F	450°F	% of Retention
Flexure Strength, psi	248,700	189,800	76%
Flexure Modulus, psi	18.1×10^6	16.9×10^6	93%
Shear Strength, psi	16,300	9,000	55%

PMR CHEMISTRY

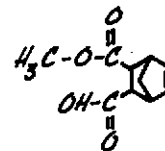
PMR CONSTITUENTS



4,4'
METHYLENEDIANILINE
(MDA)

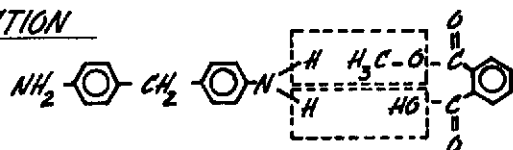


DIMETHYL ESTER OF 3,3',4,4'
BENZOPHENONE TETRACARBOXYLIC ACID
(BTDE)

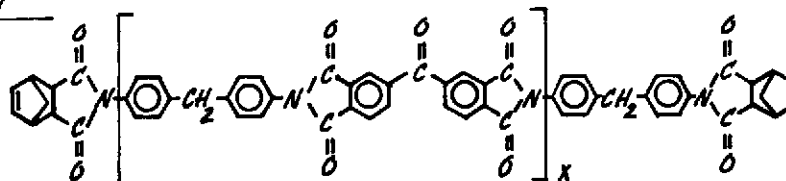


MONOMETHYL ESTER OF
5-NORBORNENE-2,3
DICARBOXYLIC ACID
(NE)

IMIDIZATION REACTION



AFTER IMIDIZATION



REPEATING UNIT

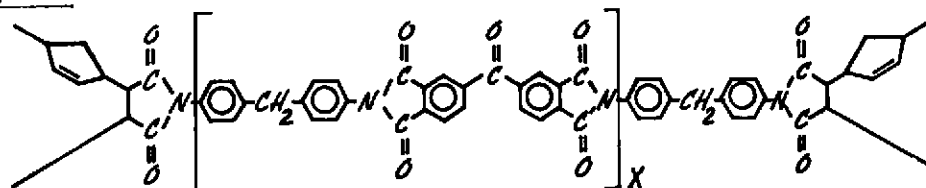


Figure 1. - PMR polyimide chemistry.

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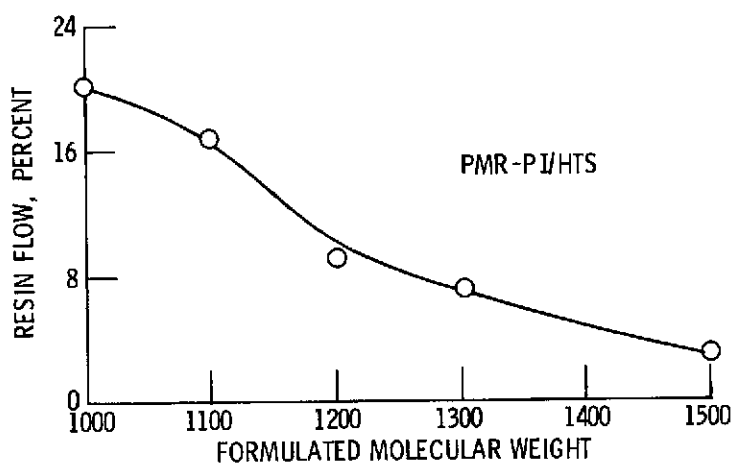


Figure 2 - Percent resin flow vs. formulated molecular weight.

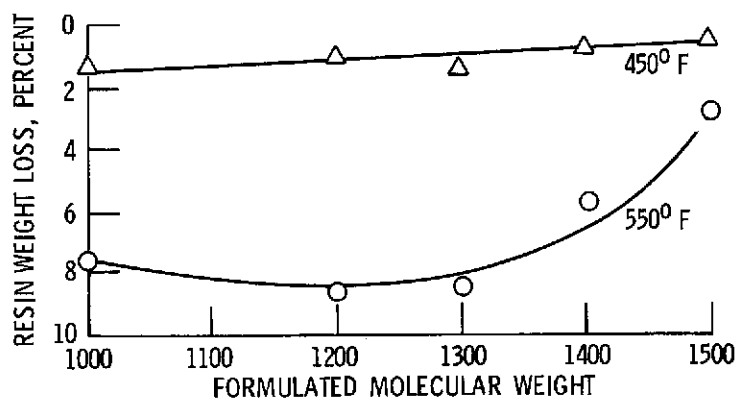


Figure 3 - Isothermal resin weight loss of PMR-PI/HTS composites exposed for 600 hr. in air vs. formulated molecular weight.

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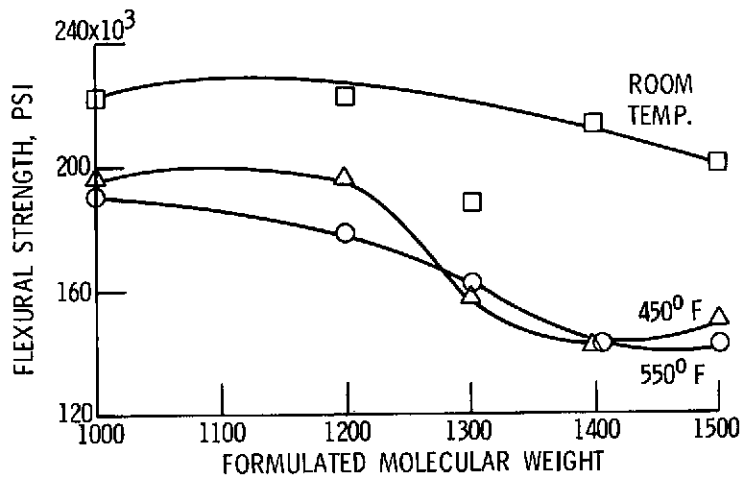
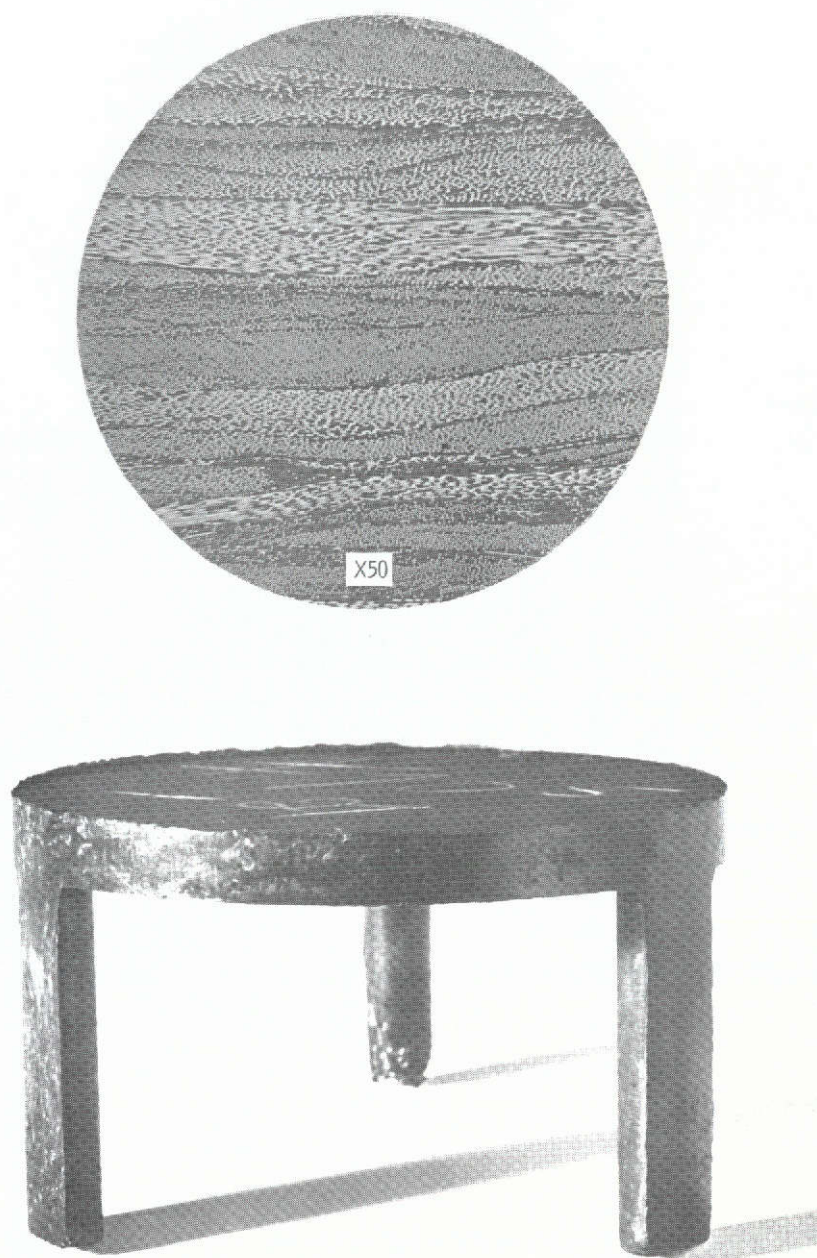


Figure 4. - Flexural strength of PMR-PI/HTS composites. Tests conducted at room temperature and at 450° and 550° F after short-time exposure at indicated test temperature.

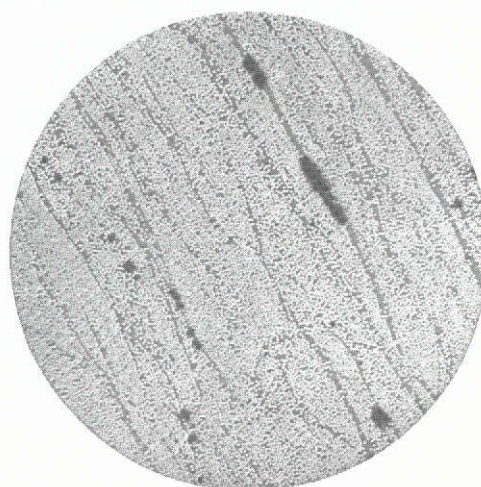
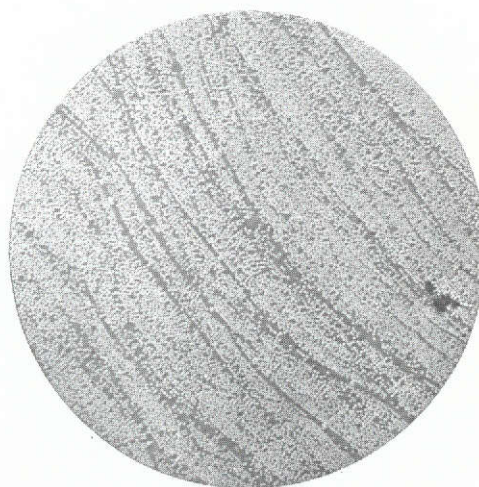
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PROPERTIES:	FLEXURE STRENGTH	40 000 PSI	FIBER: LENGTH	3/8 IN.
	FLEXURE MODULUS	4×10^6 PSI	LOADING	57.5 V/O
	TENSILE STRENGTH	15 000 PSI		

Figure 5. - PMR-15/HT-S random fiber molding.

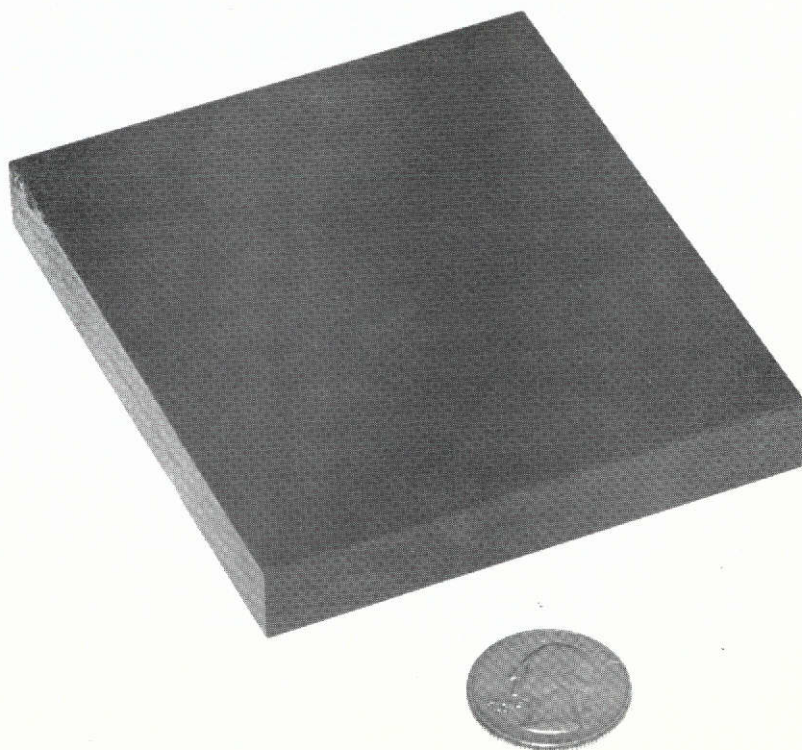
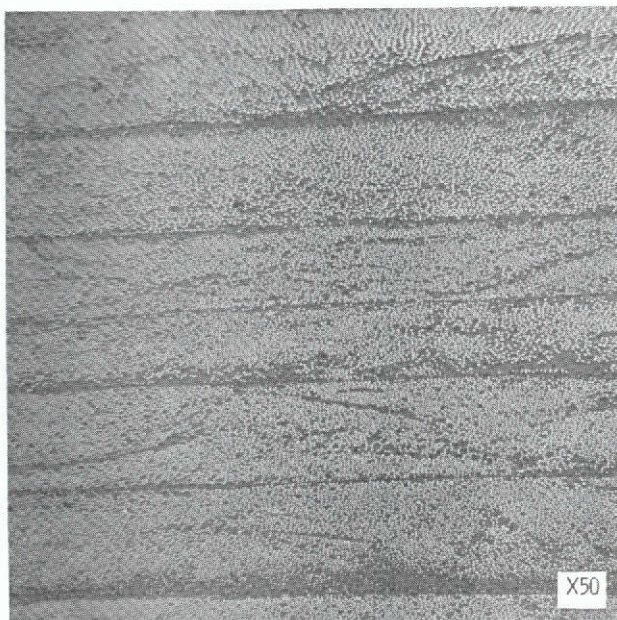
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FLEXURE STRENGTH	152 300 PSI
FLEXURE MODULUS	19.3×10^6 PSI
SHEAR STRENGTH	6100 PSI
FIBER FRACTION	0.56
SPECIFIC GRAVITY	1.58
VOID CONTENT	2.7 PERCENT

Figure 6. - Properties of autoclave cured PMR-15/HM-S composites.

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Figure 7. - PMR-15/HT-S thick laminate.

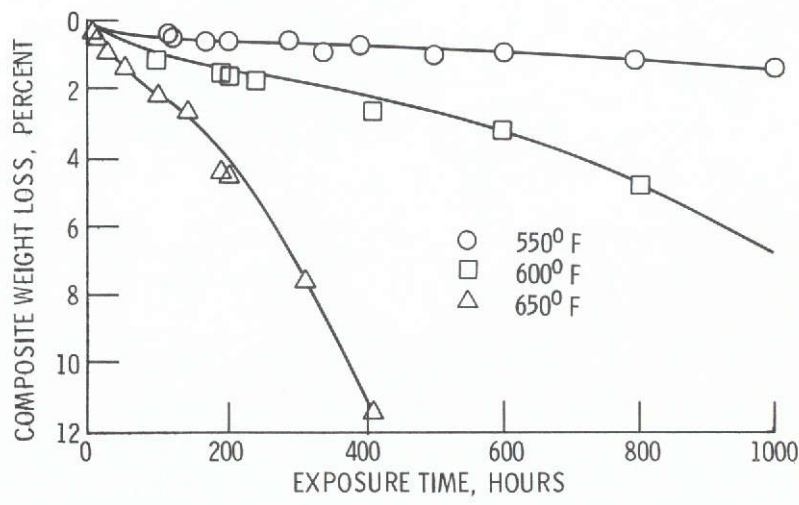
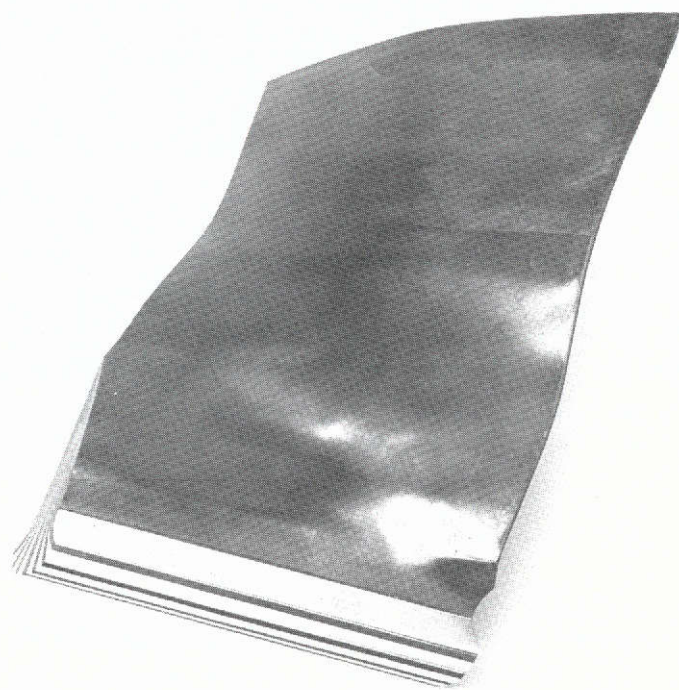


Figure 8. - Percent weight loss of PMR-15/HM-S composites exposed to 100 MI/min air flow at temperatures shown.



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Figure 9. - PMR-15/HT-S ultra-high tip speed fan blade in finished machined form.

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